

UNITED STATES PATENT OFFICE

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METHOD OF COATING SUBSTANCES

No Drawing.

Application filed September 20, 1927. Serial No. 220,831.

This invention relates to a method of coating substances with metal or metals of the alkali or alkaline-earth groups, and with the oxids of such metals. The invention is more particularly applicable to the formation of electron-emitting elements or cathodes (whether of the filamentary or indirectly-heated type) suitable for use in vacuum tubes such as audion tubes, X-ray tubes, and the like. Although the invention is not limited to a method of making such elements, it will hereafter be described in that connection, by way of suitable example.

Cathodes of the "dull-emitter" or Wehnelt type ordinarily consist of a platinum or other metallic core, usually in the form of a wire or ribbon, which has been coated with oxid of some metal or metals, such as barium, strontium, or the like. Several methods have heretofore been employed in the production of such cathodes. One of the older processes is to dip the wire to be coated into a solution of the nitrate of the desired metal or metals, and then decompose the nitrate by heating in an inert atmosphere in order to obtain the oxid. It is ordinarily necessary to apply a considerable number of successive coats of oxid in this manner if a uniform electron emission is to be obtained from the finished element. In another method of producing an oxid coating the heated wire is brought into contact with solid paraffine in which is suspended a considerable amount of barium or strontium carbonate, or the like. The carbonate being decomposed, an oxid coating remains. In this case, also, a large number of successive coatings are required. Still a third method is to paint or coat the wire with a solution of barium azide, and then apply heat in order to decompose the compound to metallic barium, which readily oxidizes.

Each of these methods is open to a number of objections, and presents certain definite disadvantages. In the first two methods there is not only the already mentioned necessity for applying a large number of successive coatings of oxid if a stable or uniform electron emission is desired, which is troublesome and expensive in itself, but there is the further difficulty that considerable

quantities of gas are apt to be occluded during the coating process. It is extremely difficult, or impossible, completely to remove this occluded gas during the subsequent evacuation of the tube, and this may account, to some extent, for the frequent erratic behavior of cathodes made in this way. Moreover, it is difficult to make the coatings of uniform thickness; and "hot-spots" and consequent burning out of the filament frequently occur. With regard to the third process, barium azide is a highly explosive compound; its preparation is correspondingly difficult, and the process is so dangerous as to be highly unsatisfactory.

Our invention provides a means for applying metallic or oxid coatings to substances of any desired character. The method is substantially free from the foregoing difficulties and objections, and results in a more uniform and adherent coating than has been (so far as we are aware) hitherto obtainable.

According to a preferred method of practicing our invention we first prepare a solution of the desired alkali or alkaline-earth metals in a volatile substantially anhydrous ammoniacal liquid. We then apply this metal solution to the surface of the substance to be coated, and expose the surface to the air at ordinary temperatures. The solvent quickly vaporizes, leaving a surface film of the dissolved metal or metals. This film readily oxidizes on continued exposure to the air, forming a firm, evenly distributed, uniform, and adherent coating of oxid.

A particular example of one method of carrying out our invention is as follows:

Anhydrous liquid ammonia is placed in a Dewar flask and an excess of barium metal is added thereto. A characteristic blue solution quickly results, and since the metallic barium is present in excess, there may be a second and more concentrated phase, for example in the nature of a suspension, as well. It has been established, as we believe, that the barium is present in an ionized condition, since free electrons are liberated in the solution. This solution is then applied, by dipping, painting, or otherwise, to the surface of a filament wire, for example, which it is

desired to coat. The filament is exposed to the air so that the ammonia will vaporize. A surface film of metallic barium then remains. This may be utilized directly for certain purposes, but is readily oxidized by further exposure to the air, in which case an oxid skin or coating having the generally desired properties is formed. In some cases we prefer to heat the filament, as by passing an electric current through it, in order to bring about an even firmer bond between the oxid coating and the metal. The necessity for this heat treatment, as well as the optimum temperature and duration, depends somewhat upon the metal to which the coating is applied and the oxid or oxids which compose the coating. Obviously, the exact conditions cannot be specified in advance, but may be readily determined for any given case.

As an alternative to anhydrous liquid ammonia as a solvent, we have found that certain alkyl amines, for example methyl amine and ethyl amine, may be employed successfully as solvents. We regard such solvents as substantially equivalent, for the purposes of the present invention, to liquid ammonia. The term "ammoniacal liquid" as used in this application either in the specification or claims is to be understood, therefore, as including the several alkyl amines as well as liquefied ammonia.

It is not essential to our invention that the metal or metals employed shall be directly dissolved in the solvent, since other methods of producing a metal solution of the character described are equally applicable. For example, a solution in ammonia of a salt of the desired metal or metals may be subjected to electrolysis in order to produce the required metal solution.

The metal barium is one example only of the several metals which may be treated according to our invention. Metals of the alkali group, such as sodium, potassium, cesium, etc., etc.; and metals of the alkaline-earth group such as strontium, calcium, etc., which are readily oxidized, are soluble in liquid ammonia and form electron emitting oxides, are all suited for use according to our process. The term, oxidizable metal, as used in the specification and claims is to be understood as including the alkali metals as well as the metals of the alkaline earths. We frequently employ solutions containing several of these metals, for example, barium, strontium, and calcium, etc., or barium, cesium, potassium, etc.; or we may apply alternate coatings derived from different solutions; for example, an alkaline-earth oxid or oxids in alternation with oxid or oxids of alkali metals.

With regard to the object or substance which is to receive a metallic or oxid coating, we may employ a metal in the form of a wire, filament, ribbon, small tube or rod, plate, or

the like. We have found that nickel, or nickel-chromium alloys, are good examples of metals which act satisfactorily in receiving and retaining the coating. Even more refractory metals, such as tungsten, molybdenum, tantalum, platinum, etc., are also suitable. Our invention, however, is not confined to coating metals or metallic substances. In some cases we wish to apply a metal or oxid coating to a non-metallic substance such as porcelain, silica, and so forth. There are certain types of cathodes (used in the so-called "heater" tubes) in which the emitting surface is not identical with the heating element, but comprises a tube or small cylinder, etc., which is heated by means of a separate filament or heater arranged within it. Our invention is equally applicable to coating such emitting elements intended to be separately heated, and may be applied to them whether they are of metallic or non-metallic composition.

It will be clear from the foregoing description that our process is susceptible of many variations and modifications, all of which come within the spirit of our invention.

We claim:

1. Process of coating substances with at least one of the metals from the group consisting of the alkali metals and the alkaline earth metals which comprises treating the metal with substantially anhydrous liquid ammonia, applying the resulting metal solution to the substance to be coated, and driving off the ammonia to leave a coating containing the metal.

2. Process of coating substances with an electron-emitting oxid of a metal from the group consisting of the alkali metals and the alkaline-earth metals, which comprises treating the metal with substantially anhydrous liquid ammonia, applying the resulting metal solution to the substance to be coated, and converting the resulting coating to oxid.

3. Process of coating substances with an electron-emitting oxid material derived from a plurality of metals from the group consisting of the alkaline metals and the alkaline-earth metals, which comprises treating the metals with substantially anhydrous liquid ammonia, applying the resulting metal solution to the substance to be coated, and converting the resulting coating to oxid.

4. Process of coating substances with a plurality of electron-emitting oxides of metals from the group consisting of the alkali metals and the alkaline-earth metals, which comprises forming a plurality of solutions of different metals in substantially anhydrous liquid ammonia, said metals being from the group consisting of the alkali metals and the alkaline-earth metals, successively applying the resulting metal solutions to the substance to be coated, and converting the resulting coatings to oxid.

5. Process of coating a metallic element of refractory character with electron-emitting oxid material to form an electron-emitting cathode element, comprising treating at least one of the metals from the group consisting of the alkali metals and the alkaline-earth metals with substantially anhydrous liquid ammonia to form a solution, applying the resulting metal solution to the element to be coated, and converting the resulting coating to oxid.

6. Process of coating a metallic element of refractory character with electron-emitting oxid material to form an electron-emitting cathode element, comprising treating at least one of the metals from the group consisting of the alkali metals and the alkaline-earth metals with substantially anhydrous liquid ammonia to form a solution, applying the resulting metal solution to the element to be coated, and converting the resulting coating to oxid by driving off the ammonia and heating the coated element in an oxidizing atmosphere.

7. Process of coating a substance with barium oxid, which comprises treating barium metal with substantially anhydrous liquid ammonia, applying the resulting barium solution to the substance to be coated, and converting the resulting coating to barium oxid.

8. The method of producing objects having an electron-emitting coating which comprises treating readily oxidizable metal with substantially anhydrous ammoniacal liquid solvent so as to form a composition more fluid than the metal, applying the composition to the object so as to form a coating, evaporating the solvent, and converting the metal to oxide.

9. The method of producing objects having an electron-emitting coating which comprises wetting the object with a solution of a readily oxidizable metal in a substantially anhydrous ammoniacal liquid, evaporating the solvent, and converting the metal to oxide.

10. The method of producing objects having an electron-emitting coating containing an oxide of an alkaline earth metal which comprises treating the metal with substantially anhydrous ammoniacal liquid so as to form a composition more fluid than the metal, applying the composition to the object so as to form a coating, and converting the metal to oxide.

11. The method of producing objects having an electron-emitting coating containing an oxide of a readily oxidizable metal which comprises treating the readily oxidizable metal with substantially anhydrous liquid ammonia so as to form a composition more fluid than the metal, applying the composition to the object so as to form a coating,

evaporating the solvent, and converting the metal to oxide.

12. The method of producing objects having a coating containing an oxide of an alkaline-earth metal which comprises treating the metal with substantially anhydrous liquid ammonia so as to form a composition more fluid than the metal, applying the composition to the object so as to form a coating, evaporating the ammonia, and converting the metal to oxide.

13. The method of producing objects having an electron-emitting coating containing an oxide of barium, which comprises treating barium with substantially anhydrous liquid ammonia so as to form a composition more fluid than barium, applying the composition to the object so as to form a coating, evaporating the ammonia, and converting the barium to oxide.

In testimony whereof, we affix our signature.

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